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## Influence of hole extraction efficiency on the performance and stability of organic solar Cells

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### ABSTRACT

We demonstrate the impact of the hole extraction efficiency on the device performance and stability of organic solar cells. We present results on organic solar cells prepared with a poly(aniline) (PANI) based hole transport layer (HTL) blended with varying concentrations of poly(styrene sulfonate) (PSS), leading to differences in the HTL transmittance and conductivity. The PANI to PSS ratios investigated here were 1:1, 1:2 and 1:5. The initial power conversion efficiency of the devices is demonstrated to depend directly on the HTL conductivity, showing increasing performance with decreasing PSS content. However, after degradation of encapsulated solar cells under illumination, it is observed that the higher PSS content results in better stability. Data from impedance spectroscopy offers detailed insight into the interface properties, and detailed equivalent circuit analysis allows us to correlate the decreased hole extraction capabilities to the HTL properties and to the power conversion efficiency of the solar cell.

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### 1. Introduction

The future need for renewable energies to substitute current fossil energy resources drives intensive research on solar cells [1]. Organic solar cells are a promising technology, as they can be produced at low cost using roll-to-roll techniques and therefore offer short energy payback times [2,3]. Additionally, record efficiencies of organic solar cells exceeding 10% have recently been published [4,5]. In order to reach competitive performance increasing efforts on understanding efficiency limiting mechanisms and improving the device lifetime of organic solar cells are necessary for bringing this technology successfully onto the market.

Interlayers and interfaces play an important role in organic solar cells, both in terms of performance and stability [6–8]. In order to improve charge extraction efficiency from the device, selective transport layers for electrons and holes are placed between the active layer and the respective electrodes. A large quantity of novel materials has been investigated as charge transport layers, but only a few publications to date deal with their impact on device stability [9–12]. The water based dispersion poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), which is widely used as hole transport layer in organic solar cells is known to limit device stability [13–16]. The acidic nature of

the PSS within the HTL was identified as a degradation agent, but the influence of PSS concentration in the HTL on the overall device stability is complex [17]. PSS is an intrinsically insulating species which enhances the transmittance and reduces the conductivity of the HTL. A high PSS concentration lowers the pH of the HTL dispersion, and it has been shown that in solar cells with standard geometry PSS causes etching of indium and tin fractions from the widely used tin-doped indium oxide (ITO) electrode, which are then migrating into the PEDOT:PSS layer reducing its hole extraction capabilities [18,19]. On the other hand, the PSS protects the PEDOT against oxidation, acting as the negative counter ion to the positively charged polymer species. In PEDOT:PSS films, it was shown that the PSS forms a thin layer around the PEDOT particles, stabilizing the polymer against oxidation [20].

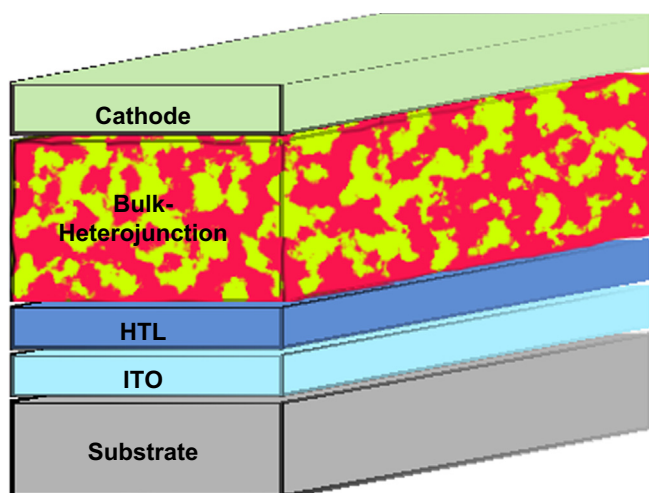
In addition to PEDOT, poly(aniline) (PANI) and PANI:PSS dispersions have been investigated as HTLs in organic optoelectronics due to the high conductivity, easy handling and stability of the polymer [21–25]. In this study we investigate the influence of the PSS content in PANI:PSS HTLs on the hole extraction efficiency and on the stability of organic solar cells. Three poly(aniline):poly(styrenesulfonate) (PANI:PSS) formulations with varying concentrations of PSS (1:1, 1:2 and 1:5) were investigated in bulk heterojunction solar cells with P3HT:PCBM active layers. In freshly prepared devices, the power conversion efficiency increases with decreasing PSS content, corresponding to the increasing conductivity of the hole transport layer. Interestingly, however, increasing the PSS content was observed to enhance the solar cell stability considerably, and devices with a higher PSS

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**Table 1**  
Properties of spin coated hole transport layers prepared with different composition.

Hole transport layer	measured PANI:PSS ratio	Thickness [nm]	Transmittance [%]	Conductivity [S/cm]
PANI:PSS 1:1	1:1.4	33	90	4.0 E-02
PANI:PSS 1:2	1:2.2	45	91	2.0 E-04
PANI:PSS 1:5	1:5.1	51	95	2.0 E-05



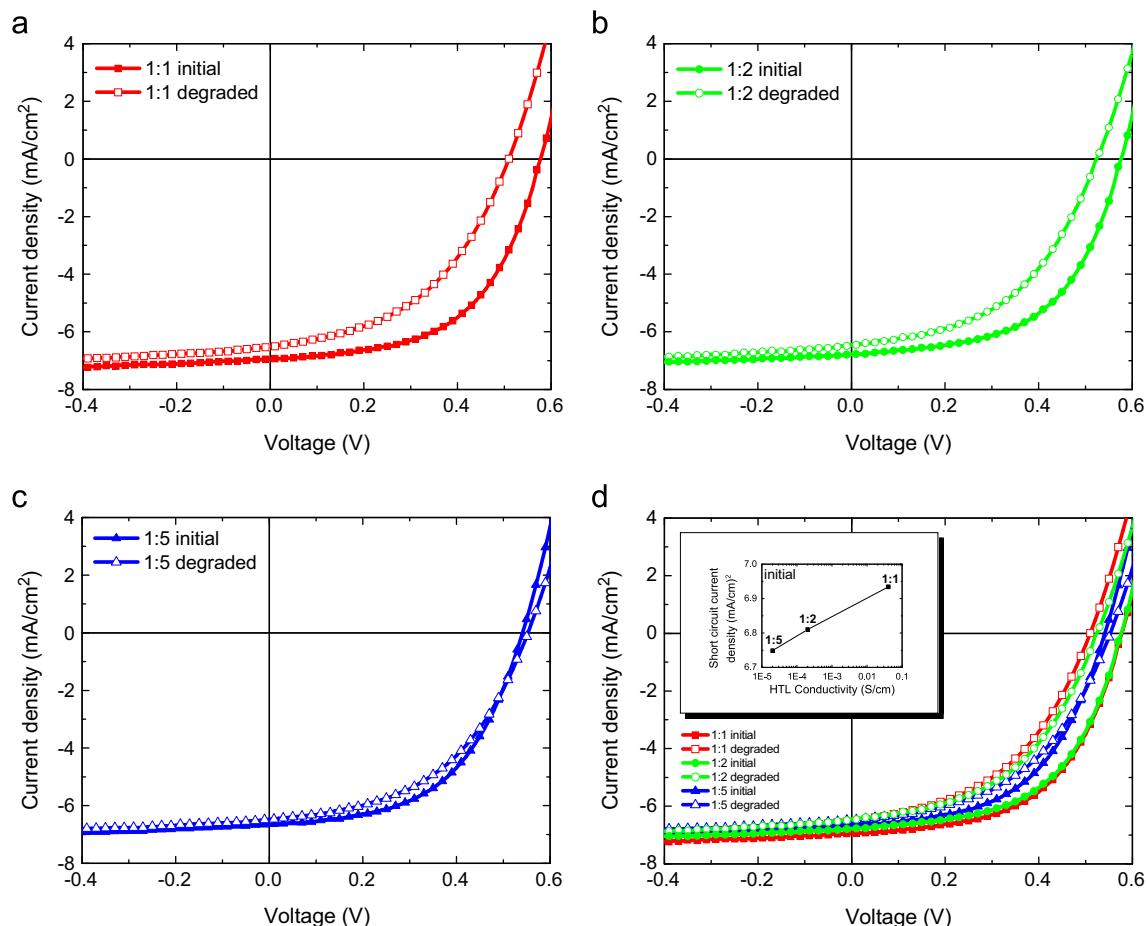
**Fig. 1.** Device structure of organic solar cells containing either one of the hole transport layer (HTL) shown in Table 1.

content demonstrate little performance loss compared to devices with low PSS content. Applying impedance spectroscopy and equivalent circuit analysis we are able to link the power conversion efficiency of the organic solar cells directly to the conductivity and stability of the hole transport layers, which determines the hole extraction efficiency within an operating solar cell [26]. These results indicate that the properties of the HTL are significant for both solar cell performance and long term stability.

## 2. Materials and methods

Poly(3-hexylthiophene) (P3HT, Rieke Metals Inc.) and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM, Solenne B.V.) were blended in *o*-dichlorobenzene in a ratio of 2:1. The mixture was stirred at 80 °C for optimal dissolution prior to the thin film deposition. PANI:PSS dispersions (Enthone GmbH), parameters summarized in Table 1, were applied by spin coating on structured, cleaned and plasma etched ITO substrates (Präzisions Glas & Optik GmbH) to form the hole transport layer.

The P3HT:PCBM bulk-heterojunction active layer was spin coated on top of the hole transport layer within a glove box and the resulting films were annealed at 140 °C for 10 min. Finally, the samples were brought into an evaporation chamber directly connected to the glove box, and a Ca/Al cathode was thermally evaporated on top of the active layer leading to a final device structure as shown in Fig. 1. In order to neglect extrinsic influences, such as ambient air and humidity on the device performance on the device stability, all solar cells were encapsulated directly after preparation in the inert atmosphere by applying epoxy glue and a



**Fig. 2.** IV characteristics of solar cells with different hole transport layers before and after degradation. The inset shows the initial short circuit current density vs. HTL conductivity.

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